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Original Article

Polyphenolic content and in vitro antioxidant characteristics of wine industry and other agri-food solid waste extracts

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Abstract

Solid by-products from white and red wine industry were subjected to evaluation as potential sources of antioxidant phytochemicals on the basis of their content in phenolics and in vitro antioxidant activity. Furthermore, several other common plant solid wastes, including apple, potato and onion peels, as well as carob pods and olive tree leaves were also considered, in order to carry out a comparative assessment. The results showed that extracts from grape seeds (either white or red) contain exceptionally high amounts of total polyphenols (10.3–11.1% on a dry weight basis), a great part of which is composed of flavanols. Red grape pomace and stems contained appreciable amounts of polyphenols, whereas potato and white grape peels were the tissues with the lowest polyphenol content. The in vitro antiradical activity and reducing power were shown to be highly dependent on the total flavonoid and total flavanol content ($P<0.001$), but the hydroxyl free radical scavenging activity did not exhibit the same trend, suggesting dependence on particular structural features. The results indicate that wine industry by-products, including grape seeds but also red grape pomace and stems, are very rich sources of antioxidant polyphenols compared with other agri-food solid wastes, and therefore their exploitation as a source of added-value products may be more cost-effective and merits a profounder investigation.

Keywords: Added-value products; Antiradical activity; Apples; Carobs; Flavonoids; Grape pomace; Olive tree leaves; Onions; Polyphenols; Potatoes; Reducing power; Vinification by-products

1. Introduction

Large quantities of both liquid and solid wastes are produced annually by the food processing industry. These waste materials contain principally biodegradable organic matter and their disposal creates serious environmental problems. The waste loads at the processing plant can be significantly reduced through the use of new or modified processing methods or through in-plant treatment and reuse, and a variety of processes are being developed towards this direction, aiming at converting the waste materials into bio-fuels, food ingredients and other added-value bio-products.

Wine industry wastes, which consist mainly of solid by-products, include marcs, pomace, and stems, and may account on average for almost 30% (w/w) of the grapes used for wine production. All these by-products may bear a considerable burden of phenolic components (González-Paramás et al., 2004), depending on the type of grape (white or red), the part of the tissue (skins, seeds, etc.), as well as the processing conditions (e.g., pomace contact). Over the past few years, not only vinification by-products, but also a number of other agricultural wastes of plant origin have attracted considerable attention as potential sources of bioactive phenolics, which can be used for

Abbreviations: AAE, ascorbic acid equivalents; A_{AR}, antiradical activity; CTE, catechin equivalents; GAE, gallic acid equivalents; P_R, reducing power; QTE, quercetin equivalents; SA_{HFR}, hydroxyl free radical scavenging activity; TFl, total flavanols; TFd, total flavonoids; TP, total polyphenols; TRE, Trolox® equivalents; S.D., standard deviation.

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various purposes in the pharmaceutical, cosmetic and food industry. However, in many instances there is a rather significant lack of appropriate feasibility studies on the exploitation of such wastes, and as a result their utilization is still in its infancy.

Studies regarding vinification by-products are mainly focused on the polyphenolic composition of seeds, which are very rich in flavanols (Yilmaz and Toledo, 2004; Guendez et al., 2005), but pomace, which is composed of seeds and skins, has also been evaluated as a potential source of antioxidant polyphenols (Alonso et al., 2002; Louli et al., 2004; Kammerer et al., 2005; Pinelo et al., 2005). On the other hand, some other parts of grape clusters that are discarded during the vinification process, such as stems, have been given much less attention, although they contain an important amount of polyphenols (Alonso et al., 2002; Souquet et al., 2000).

The examinations underlying value assessment of food plant wastes are mainly based on the content and profile of phenolics, as well as their in vitro antioxidant potency, but the wide spectrum of analytical techniques employed for both polyphenol analysis and antioxidant activity measurement make critical comparisons impractical or even problematic. The objective of this study was an assessment of several winery wastes as sources of polyphenolic antioxidants on a comparative basis with several other common food wastes. Comparisons were based on indices pertaining to the polyphenolic composition, including the determination of total polyphenols (TP), total flavonoids (TFd) and total flavanols (TFl), and their association with antioxidant activity, as this was revealed by three representative in vitro tests.

2. Materials and methods

2.1. Chemicals

Folin–Ciocalteu phenol reagent and ascorbic acid were from Fluka (Steinheim, Germany). Trolox®, gallic acid, luminol, 2,4,6-tripyridyl-*s*-triazine (TPTZ), 2,2-diphenylpicrylhydrazyl (DPPH$^{\cdot}$) stable radical, p-(dimethylamino)-cinnamaldehyde (DMACA), quercetin and catechin were from Sigma Chemical Co (St. Louis, MO, U.S.A.). Citric acid, sodium nitrite, cobalt chloride ($CoCl_2{\cdot}6H_2O$), hydrogen peroxide, Na_2-EDTA and aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$) were from Merck (Darmstadt, Germany).

2.2. Plant solid wastes

Analytical details about the plant food by-products used in this study are given in Table 1. White and red vinification by-products were from Roditis and Agiorgitiko cultivars (*Vitis vinifera* sp.) respectively, obtained from wineries in the regions of Koropi and Nemea (prefectures of Attica and Korinthia, Greece). Olive leaves were harvested from an olive tree plantation (Attica). Deseeded and chopped carob pods (kibbles), of approximately 1.5–2 mm diameter, were obtained from a carob-processing factory (Chania, Crete). Potatoes, red onions and apples were purchased from a local food store and peeled immediately after receipt. All plant material was stored at −40 °C.

2.3. Extraction procedure

A suitable quantity of tissue ranging from approximately 2–7 g was chopped into small pieces with a sharp, stainless steel cutter to facilitate extraction. The chopped tissue was ground with sea sand and a small portion of the extraction solvent, which consisted of 0.1% HCl in methanol/acetone/water (60/30/10, v/v/v), with a pestle and a mortar, and then left to macerate for 30 min in the dark, covered with a nylon membrane to minimize contact with air. The paste that formed was placed in a 100 mL conical flask with 25 mL of solvent, and extraction was performed under stirring at 700 rpm on a magnetic stirrer for 10 min. The extract was filtered through a paper filter; this procedure was repeated twice more. The extracts were then combined in a 100 mL volumetric flask, made to the volume, and

Table 1
Agri-food wastes used in this study

Plant material[a]	Tissue analysed	Moisture content (%)
White grape	Pomace (peels and seeds)	71.56
Red grape	Pomace (peels and seeds)	55.62
White grape	Stems	60.38
White grape	Seeds	45.04
Red grape	Seeds	41.56
White grape	Peels	75.28
Red grape	Peels	55.50
Olive tree leaves (*Olea europaea*)	Whole tissue	48.79
Apples (red skinned) (*Malus domestica*)	Peels	81.68
Onion (red skinned) (*Allium cepa*)	Outer dry and semi-dry layers and apical trims	88.73
Potato (brown skinned) (*Solanum tuberosum*)	Peels	81.83
Carob (*Ceratonia siliqua*)	Kibbles	11.51

[a]All grape by-products used in this study came from *Vitis vinifera* cultivars.